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Charles E. Taylor, et al

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ABSTRACT

A spark source mass spectrometer that uses electronic detection and a dedicated data analysis system was applied to a survey type trace analysis for chemical elements. Errors in the data system software were identified and corrected. Modifications to the system permit identification and quantitation of 72 elements at the part per billion level in water samples.

CONTENTS

		Page
Abstract		ii
List of Figures		iv
List of Tables		v
Acknowledgements		vi
Sections		
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Experimental	4
V	Results and Discussion	8
VI	References	23

FIGURES

No.		Page
1	Accurate Mass Data	9
2	Original Interpretation of Data	10
3	Modified Interpretation of +1 and +2 Ion Data	12
4	Sample #1 Bar Graph	14
5	Sample #2 Bar Graph	15

TABLES

No.		Page
1	Group I Coefficients of Variation	16
2	Group II Coefficients of Variation	17
3	SS Analysis of Effluent Sample	18
4	Relative Sensitivity Study in Sediment Sample	19
5	SS Analysis of Reservoir Water	21

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SECTION I

CONCLUSIONS

Survey type analysis for trace elements in natural samples can be accomplished using spark source mass spectrometry (SSMS). Weight ratios of up to 100:1 in synthetic samples showed no detrimental effect on spark source data. Valid results have been obtained for multi-element analyses of sediments. The concentration of elements in sediments ranged from the percentage level to the part per million level. Using the modified software programs and existing SSMS equipment, 72 naturally occurring elements can be identified and quantitated at the part per billion (ppb) level in water samples.

SECTION II

RECOMMENDATION

Spark source mass spectrometry should be used for survey multielement analyses to clearly and rapidly identify problem elements in the environment. Because spark source is not so limited by interference, it should also be used as a back-up for more limited analytical techniques, such as atomic absorption and emission spectroscopy.

SECTION III

INTRODUCTION

Any elements or their compounds are pollutants if they occur at concentrations that adversely affect water usage. Because these concentrations may be very low, a method of trace analysis for a broad survey of chemical elements is essential to pollution monitoring. Emission and atomic absorption spectroscopy are each currently used for such applications. However, using emission spectroscopy, one can routinely analyze for only 18-20 elements; atomic absorption is even more limited. The spark source mass spectrometer with its related data system combines sensitivity and broad range analysis capability with convenient analysis time. To assess the applicability of spark source mass spectrometry to the analysis of water and sediments we conducted this study evaluating a new computerized electronic detection system.

SECTION IV

EXPERIMENTAL.

The instrument used was an AEI MS 702 spark source mass spectrometer equipped with electronic detection. Accessories allow either peak switching or scanning for data collection.

Peak switching is used when the analyst is interested in a more precise recording of a few peak intensities than is provided by a normal scan. It is used when major interest is in 2 or 3 elements. Switching is also used when isotopic dilution methods are required for ultimate accuracy in spark source (SS) analyses. Scanning is a survey analysis application and can include the total spectrum to encompass all known isotopes. The less precise measurements obtained from scanning are acceptable when the analyst requires a rapid survey, trace analysis system.

The spark source mass spectrometer is equipped with an AEI data reduction system; this includes a SS interface, a Digital Equipment Corporation (DEC) PDP8/e 4K Computer, a 12-bit A/D Converter, a DF 32 and DS 32 disc memory, a teletype and high speed reader/punch and vendor-supplied DS-40 software. All data to be discussed were taken using the electronic detection and data system. The data system is functional only when the SS system operates in the scanning mode. The DS-40 software is not equipped for photographic plate or peak switching data.

Calibration standards and other synthetic samples used to obtain relative sensitivites and to check out the

system were made up from commercially available metals, powders, and solutions. Standard samples were mixed in solution and dried onto high purity graphite. The graphite-sample was mixed using a Spex mill and pressed into electrodes using an AEI die and polyethylene slugs.

Although graphite was a very good matrix for electrode material, it presented some problems to the original software. The complex ions, C_2^+, C_3^+, ..., C_{20}^+ (composed of both isotopes, ^{12}C and ^{13}C) caused false elemental identification and some erroneous quantitative data. Changes of analytical and confirmatory mass-to-charge ratios (m/e's) were required in the software. The necessary changes were made as single element tapes that replaced original software data on the disc memory system.

Relative sensitivities were determined in a series of samples that contained yttrium and one or more of the 70 elements of interest in equal portions by weight. Using yttrium as the internal standard, the relative sensitivity data were combined with the weight conversion factor to yield the parameter K in the concentration equation (Equation 1).

Equation 1
Concentration Calculation

$$\frac{A_{el}}{A_{std}} \times \frac{F_{std}}{F_{el}} \times C_{std} \times K = \text{Concentration}$$

where A_{el} = Area of analytical isotope of element in question

A_{std} = Area of analytical isotope of standard

F_{el} = Abundance factor of element in question (100/isotopic abundance of analytical isotope)

F_{std} = Abundance factor of standard (100/isotopic abundance of analytical isotope)

C_{std} = Concentration of standard element. The units used to express the standard concentration value define the units of "concentration," since the remainder of the equation is unitless.

K = [weight conversion factor × relative sensitivity]

Weight conversion factor = a.m.u. element/a.m.u. standard

Using standards in various mixtures of elements and in various concentration ranges, we identified two major problems with the original data system software supplied by the vendor. Multiply-charged ions are very important in SS analysis using electronic detection since the low resolution inherent in this mode of operation does not allow reliable isotope ratio confirmation. False interpretations in some analyses were made by the data system when ions of +2 and/or +3 charges (+2 and/or +3 ions) were used as the analytical m/e or the confirming multiply-charged ion. This problem occurred at masses of $\leq$ 80 amu, where +2 and +3 ions may occur.

The original software used a $\pm$ 0.2 amu tolerance to accept or reject a singal as the analytical or confirming mass of a given element. For example, for an iron analysis at 56 amu, the computer-calculated signal had only to fall between 55.8 amu and 56.2 amu to be accepted at the ^{56}Fe. The tolerance window of $\pm$ 0.2 amu was changed to $\pm$ 0.09 amu, a figure based on tests involving a series of standards. Samples of elements at a 100:1 weight ratio were used for this test. The complex spectra in the $\leq$ 80 mass

range yielded no false analyses using the ± 0.09 amu tolerance.

Changing the tolerance window brought to light another, less obvious, problem. Using the ± 0.09 tolerance, we found that isotopic weight values in one subroutine had been programmed using nominal instead of accurate mass values, e.g., 89 instead of 88.91 for Y. The programming was not consistent, since some subroutines of the software used accurate mass values. When the ± 0.09 amu tolerance was applied, the error had to be corrected. Further explanation of the interpretation details[2,3,4] is in the literature and will not be fully explored here.

Incorporation of all software changes were made, and the revised program was copied onto punched tape using a SERL Disc Dump/Restore tape and DEC-08-YXiA-PD-Binary Punch Teletype tape. The modified program now can be loaded into the data system in about 10 minutes compared to 45 minutes for the original software. The present program does not require manual changes of any values; the original program required 6 hours of manual entry of necessary changes.

SECTION V

RESULTS AND DISCUSSION

Equation 1 is used in the software for analytical calculations. The values in the original software were converted from ppm atomic to a weight basis by making K a product of the weight conversion factor and the relative sensitivity of the element in question.

Figure 1 is an accurage mass listing of a complex synthetic sample. Peaks are numbered (Pk.No.) starting with the highest mass detected, designated "1", down to the lowest mass, assigned the highest peak number. The normalized intensity (Norm.Inty.) is the integrated peak area normalized to the peak with the greatest raw intensity in the recorded spectrum. The accurate masses (Acc.Mass.) are calculated for each peak using the operator-supplied reference peaks, indicated by the letter (R) to the right of the accurate mass data. This part of the program was the portion of the original software that used accurate masses and was incompatible with the nominal values in the data interpretation program discussed earlier.

Figure 2 shows interpreted data as processed by the original software. The column heading "Mass" denotes the analytical m/e. "Element" is the corresponding element. "PPM atomic" is the concentration expressed in ppm on an atomic basis. "++?" "+++?" indicates the confirmation or non-confirmation of am element determined by the presence or absence of the multiply-charged ions. "Confirm isotopes" indicates whether or not a specified ratio of a given set of isotopes has been found for the

Figure 1
Accurate Mass Data

PK. NO.	NORM. INTY.	ACC. MASS
1	11	278.85
2	74	277.18
3	10	261.82
4	34	260.85
5	43	245.94
6	156	244.69
7	9	238.72
8	13	231.82
9	985	230.38
10	19	219.14
11	9	217.93
12	818	216.96
13	9	209.48
14	11	208.49
15	16	207.34
16	5	206.38
17	61	205.33
18	13	204.41
19	69	204.15
20	238	198.85
21	3574	197.82
22	1163	196.89
23	9189	194.98
24	1388	193.99
25	77	192.94
26	853	191.97 R
27	18	191.82
28	4	190.83
29	9	189.78
30	25	188.92
31	159	186.88
32	4	184.78
33	9	183.89
34	81	182.86
35	30	181.89
36	488	180.89
37	851	179.95 R
38	27	178.88
39	9	177.84
40	13	176.83
41	479	175.96
42	81	174.95
43	1888	173.98
44	1483	172.94
45	1339	171.93
46	781	170.93
47	1180	169.94 R
48	4483	168.95
49	8348	167.97
50	1520	166.95
51	8191	165.93
52	4888	164.96
53	1985	163.96
54	8864	162.94
55	948	161.96
56	946	160.97
57	1454	159.93
58	4878	158.95
59	1488	157.93 R
60	737	156.93
61	1964	155.94
62	784	154.94
63	1668	153.93
64	1797	152.95
65	8119	151.93
66	1588	150.94
67	1185	149.98 R
68	1139	148.94
69	1497	147.93
70	393	146.94
71	1822	145.91
72	783	144.95
73	898	143.93
74	736	142.93
75	8116	141.91
76	3673	140.92
77	75	139.98
78	8439	138.91 R
79	9	137.91
80	72	136.88
81	281	132.93
82	874	131.98
83	46	129.98
84	43	127.98
85	88	125.88
86	9	124.84
87	11	123.86
88	84	121.86
89	845	120.93
90	648	119.91 R
91	18	118.84
92	41	117.82
93	33	116.87
94	74	115.88
95	807	114.87
96	56	113.86
97	884	112.86
98	18	111.85
99	13	110.86
100	1252	109.88
101	60	108.94
102	4227	107.91 R
103	8399	105.98
104	1937	104.98
105	3888	103.98
106	6842	102.98
107	8610	101.92
108	1796	100.91
109	1182	99.91
110	1474	98.93
111	410	98.58
112	357	97.96
113	184	97.58
114	858	97.08
115	986	96.97
116	19	94.91
117	17	93.94
118	38	92.94
119	21	91.93
120	6	89.95
121	3512	88.91 R
122	173	87.99
123	895	86.98
124	856	86.48
125	361	85.99
126	814	85.49
127	795	84.97
128	8292	84.48
129	8187	84.00
130	488	83.48
131	884	82.98
132	8918	82.48
133	576	81.99
134	880	81.49
135	385	80.99
136	387	80.48
137	585	79.97
138	8385	79.48
139	498	78.98
140	881	78.48
141	484	77.98
142	892	77.48
143	689	76.97
144	1696	76.48
145	777	75.97
146	1394	75.47
147	373	74.97
148	341	74.46 R
149	836	73.96
150	374	73.47
151	794	72.97
152	195	72.45
153	1782	71.97
154	889	71.48
155	699	70.98
156	8827	70.48
157	53	69.94
158	3948	69.44
159	181	68.93
160	93	66.42
161	19	65.95
162	111	65.63
163	46	65.09
164	185	64.96
165	84	64.68
166	33	63.91
167	17	62.98
168	39	61.92
169	438	60.94 R
170	3918	59.93
171	12	58.89
172	36	58.68
173	186	57.98
174	43	57.68
175	81	57.38
176	81	56.98
177	84	56.68
178	361	56.87
179	866	55.91
180	98	55.61
181	142	55.87
182	4438	54.87
183	181	54.68
184	48	54.38
185	648	53.93
186	86	53.61
187	65	53.38
188	1187	52.94
189	83	52.62
190	288	52.44
191	35	52.09
192	881	51.94
193	46	51.62
194	8978	51.44
195	1168	50.95 R
196	57	50.63
197	338	50.48
198	383	49.96
199	87	49.63
200	884	49.45
201	61	49.30
202	503	48.98
203	73	48.64
204	6	48.48
205	84	48.31
206	4883	47.99
207	38	47.64
208	118	47.31
209	574	46.98
210	889	46.32
211	76	45.97
212	6873	44.97
213	4838	44.47
214	548	44.00
215	18	43.46
216	8	42.58
217	89	42.48
218	16	42.28
219	35	41.99
220	16	41.84
221	112	40.98
222	8392	39.97
223	19	39.74
224	1718	38.97 R
225	67	38.88
226	7989	36.99
227	82	36.65
228	9387	36.01
229	95	35.89
230	7898	34.99
231	16	34.75
232	82	34.65
233	899	34.32
234	133	33.99
235	97	33.65
236	79	33.33
237	54	32.99
238	846	32.89
239	793	31.98
240	492	30.91
241	1872	29.67
242	423	29.01
243	7452	28.01
244	6	27.49
245	3845	27.01
246	841	26.92
247	14	25.76
248	84	25.58
249	3858	25.00
250	14	24.58
251	3982	24.04
252	83	23.49
253	6685	23.00
254	9316	22.46 R
255	44	21.99
256	12	20.99
257	4	20.49
258	8769	20.00
259	75	19.50
260	5	19.01
261	1818	18.50
262	317	18.02
263	4578	17.58
264	255	17.02
265	6482	16.01
266	173	15.49 R
267	854	14.99
268	10889	14.01
269	886	13.50
270	71	11.67
271	19	11.51
272	973	11.03
273	831	10.03
274	46	9.52
275	4579	9.08 R

INTERPRET ? :Y

Figure 2
Original Interpretation of Data

MASS	ELEMENT	PPM ATOMIC	+++?	CONFIRM ISOTOPES	CHECK OVERLAP		COMPLEX IONS
					-----NO MATRIX-----		
197	GOLD	66.73	D+	-			
195	PLATINUM	111.50	D+	YES			
193	IRIDIUM	8.18	NO	NO			
189	OSMIUM	3.81	NO	NO			
182	TUNGSTEN	1.98	NO	NO			
181	TANTALUM	9.27	NO	-			
178	HAFNIUM	.68	NO	NO			
175	LUTECIUM	.37	NO	NO			
176	YTTERBIUM	180.94	D+	YES			
169	THULIUM	77.99	D+	-			
166	ERBIUM	113.09	D+	NO			
165	HOLMIUM	89.37	D+	-			
163	DYSPROSIUM	155.98	D+	YES			
159	TERBIUM	73.68	D+	-			
158	GADOLINIUM	97.86	D+	YES			
153	EUROPIUM	98.82	D+	YES			
147	SAMARIUM	67.48	D+	NO			
146	NEODYMIUM	102.14	D+	YES			
141	PRASEODYME	66.71	D+	-			
140	CERIUM	1.48	NO	NO			
139	LANTHANUM	97.11	D+	-			
138	BARIUM	.84	NO	NO			
133	CESIUM	5.54	D+	-			
128	TELLURIUM	2.48	NO	YES			
121	ANTIMONY	7.68	NO	NO			
118	TIN	2.09	NO	YES			
115	INDIUM	3.56	D+	NO			
111	CADMIUM	1.65	D+	NO			
105	PALLADIUM	151.71	D+	NO			
103	RHODIUM	117.84	D+	-			
101	RUTHENIUM	102.76	D+	YES			
95	MOLYBDENUM	8.15	D+	YES	194(	99)	
93	NIOBIUM	.09	D+	-			
90	ZIRCONIUM	.83	NO	NO	150(	98)	
89	YTTRIUM	STANDARD					
88	STRONTIUM	3.58	NO	NO	176(	88)	
					174(	87)	
					172(	86)	
85	RUBIDIUM	19.17	D+	NO	170(	85)	
					174(	87)	
79	BROMINE	16.88	NO	YES	158(	79)	
					162(	81)	
80	SELENIUM	18.09	NO	NO	160(	80)	
					154(	77)	
					156(	78)	
75	ARSENIC	6.43	NO	-	150(	75)	
72	GERMANIUM	113.56	D+	NO	144(	72)	
					146(	73)	
					148(	74)	
69	GALLIUM	9.96	D+	NO	140(	70)	
66	ZINC	1.81	D+	YES	132(	66)	
					134(	66)	
					128(	64)	
					192(	64)	

MASS	ELEMENT	PPM ATOMIC	+++?	CONFIRM ISOTOPES	CHECK OVERLAP		COMPLEX IONS
63	COPPER	.46	NO	NO	126(	63)	
					129(	63)	
					128(	65)	
					130(	65)	
60	NICKEL	255.98	NO	NO	124(	62)	
					116(	58)	
					174(	58)	
59	COBALT	.21	D+	-	118(	59)	
					177(	59)	
56	IRON	5.85	D+	NO	168(	56)	
					108(	54)	
					162(	54)	
55	MANGANESE	76.66	D+	-			
52	CHROMIUM	16.96	NO	NO	104(	52)	
					156(	52)	
					106(	53)	
					159(	53)	
51	VANADIUM	99.82	D+	-	102(	51)	
					153(	51)	
48	TITANIUM	113.68	D+	YES	141(	47)	
45	SCANDIUM	184.68	D+	-			
40	CALCIUM	41.09	NO	NO	86(	43)	
39	POTASSIUM	32.48	D+	NO	82(	41)	
35	CHLORINE	176.86	D+	NO			
34	SULPHUR	55.88	NO	NO	102(	34)	
					66(	33)	
					99(	33)	
					96(	32)	
31	PHOSPHORUS	13.66	D+	-			
28	SILICON	141.18	NO	NO	87(	29)	
					60(	30)	
27	ALUMINIUM	55.89	D+	-			
24	MAGNESIUM	67.82	NO	NO	48(	24)	
					52(	26)	
					78(	26)	
23	SODIUM	149.38	D+	-			
19	FLUORINE	.89	D+	-	38(	19)	
					57(	19)	
16	OXYGEN	119.87	NO	-	34(	17)	
					51(	17)	
14	NITROGEN	172.81	NO	-	28(	14)	
					30(	15)	
					45(	15)	
11	BORON	80.18	NO	YES	22(	10)	
					30(	10)	
9	BERYLLIUM	78.86	NO	-			

END OF RUN

element. This column should be of little interest because of interference from other isotopes and complex ions. "Check overlap" reminds the operator of possible multiply-charged ion interferences. "Complex ions" is a printout of matrix atoms that could possibly interfere at a given m/e. These ions, in general, in a graphite matrix-water analysis are constant and this portion of the analysis is bypassed to save computer time.

The choice of a reliable analytical mass is exemplified in Figures 2 and 3. Titanium has isotopes of 46, 47, 48, 49, and 50 amu, all of which are listed in Figure 1. Since polycarbon ion interference exists at 48 and 49 amu, the choices are reduced to 46, 47, and 50 amu. Possible interfering isotopes are ^{46}Ca and ^{50}V, leaving 47 as a probable analytical mass. Possible interference exists at mass 47 from a multiply-charged ion of mass 94, which, in this case, is listed as present in Figure 1. These interferences leave only two logical choices for the analytical mass. Since ^{47}Ti is a more abundant isotope than ^{49}Ti, the other available odd number mass, the multiply-charged ^{47}Ti isotope at 23.5 amu is used for identification and quantitation.

Errors present in the use of multiply-charged ions in the original program have been corrected. These errors occurred in analyses that had detectable +2 and/or +3 ions occurring within a nominal amu (Figure 1). This error was possible because of a wide tolerance (0.2 amu) in the original software.

After the tolerance was changed to $\pm$ 0.09 amu, all masses used in data interpretation had to be changed in the software, since the original software used nominal masses for data interpretation. The differences between

Figure 3

Modified Interpretation of +1 and +2 Ion Data

JULY SEVENTEEN		CONCENTRATIONS	++? +++?	CONFIRM ISOTOPES	CHECK OVERLAP	COMPLEX IONS
197	GOLD	65.75	2+	-	-----NO MATRIX-----	
195	PLATINUM	256.66	2+	YES		
191	IRIDIUM	2.58	NO	NO		
189	OSMIUM	5.15	NO	NO		
182	TUNGSTEN	7.29	NO	NO		
175	LUTECIUM	.52	NO	NO		
172	YTTERBIUM	146.22	2+	YES		
65	THULIUM	57.23	2+	-	169(65)	
167	ERBIUM	136.39	2+	YES		
165	HOLMIUM	102.67	2+	-		
163	DYSPROSIUM	236.65	2+	YES		
159	TERBIUM	126.73	2+	-		
156	GADOLINIUM	222.27	2+	YES		
153	EUROPIUM	184.12	2+	YES		
147	SAMARIUM	116.74	2+	NO		
143	NEODYMIUM	152.42	2+	NO		
141	PRASEODYME	96.86	2+	-		
140	CERIUM	2.84	NO	NO		
139	LANTHANUM	67.81	2+	-		
138	BARIUM	.31	NO	NO		
66	CESIUM	.49	2+	-		
125	TELLURIUM	2.61	NO	YES		
118	TIN	1.69	NO	NO		
115	INDIUM	2.32	NO	NO		
111	CADMIUM	3.88	NO	NO		
105	PALLADIUM	101.65	2+	NO		
51	RHODIUM	52.31	2+	-	103(51)	
50	RUTHENIUM	77.83	2+	NO	101(50)	
95	MOLYBDENUM	1.41	NO	-	190(95)	
89	YTTRIUM	STANDARD				
43	RUBIDIUM	.66	2+	-	85(43)	
					170(85)	
26	MANGANESE	.81	2+	-	55(28)	
					82(28)	
25	VANADIUM	.78	2+	-	51(25)	
					76(25)	
24	TITANIUM	1.47	2+	NO	47(24)	
					71(24)	
23	SCANDIUM	183.97	2+	-	45(23)	
20	CALCIUM	3.66	NO	NO	40(20)	
					60(20)	
39	POTASSIUM	.21	2+	YES	39(20)	
					82(41)	
18	CHLORINE	220.39	2+	-	35(18)	
16	PHOSPHORUS	.41	2+	-	31(16)	
14	ALUMINIUM	.56	2+	-	27(14)	
12	SODIUM	.63	2+	-	23(12)	
19	FLUORINE	.93	NO	-	38(19)	
					57(19)	
16	OXYGEN	19.84	NO	-	34(17)	
					51(17)	

JULY SEVENTEEN		CONCENTRATIONS	++? +++?	CONFIRM ISOTOPES	CHECK OVERLAP	COMPLEX IONS
14	NITROGEN	27.55	NO	-	28(14)	
					30(15)	
					45(15)	
11	BORON	1.16	NO	NO	20(10)	
					30(10)	
9	BERYLLIUM	.94	NO	-		

END OF RUN

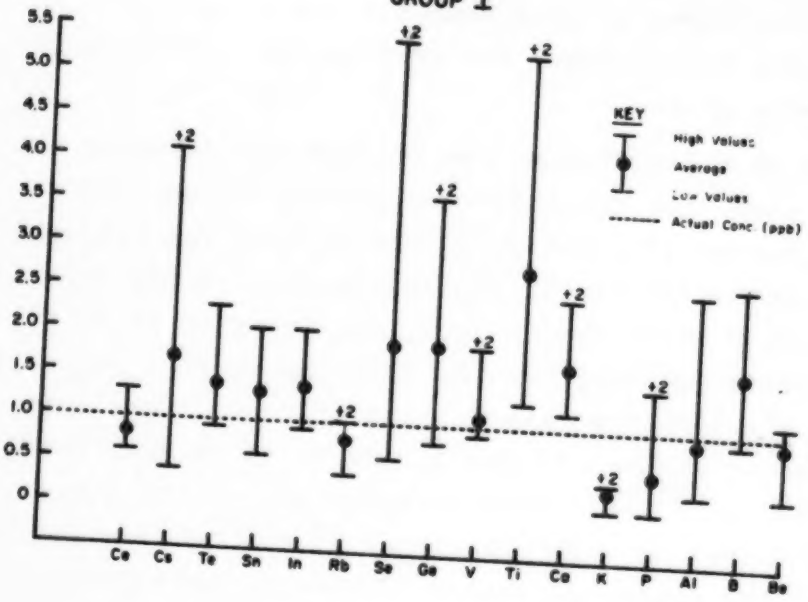
nominal mass and accurate mass calculated by the computer were in some cases greater than the new tolerance. In other cases, they allowed for very little instrumental and hardware error.

The value of these changes can be seen by comparing the accurate mass, the original interpretation, and the modified system (Figures 1, 2, and 3). In the original interpretation (Figure 2) niobium is incorrectly reported and confirmed using the +2 ion. Confirmation of +2 for niobium was supposedly made at 93/2 amu or 46.5 amu. In checking the accurate mass listing (Figure 1) the only ion occurring between 46 and 47 amu is 46.32 amu, which is a +3 ion of ^{139}La. This error is due to the $\pm$ 0.2 amu as the 46.5 amu confirmation. It can be seen in the output of the corrected system (Figure 3) that niobium is neither reported nor confirmed. This error occurred also for gallium, zinc, cobalt, and iron in the original data (figure 2).

Using the modified software system, a series of samples having highly varying concentration ratios and atomic weight differences has been analyzed. Results are shown in Figures 4 and 5. Coefficients of variation for each element are given in Tables 1 and 2. These values are based on 9 separate runs using a fresh set of electrodes for each analysis. The statistical data shown agree with those reported earlier by this laboratory.[2]

Results of the analyses of natural samples show comparable precision to the data shown in Tables 1 and 2. Tables 3 and 4 represent the analysis of an effluent sample sent to our laboratory. The sample was prepared by centrifugation. The liquid was then decanted carefully to preserve the integrity of the pellet. Two one-

FIGURE 4
SAMPLE #1
GROUP I



SAMPLE #1
GROUP II

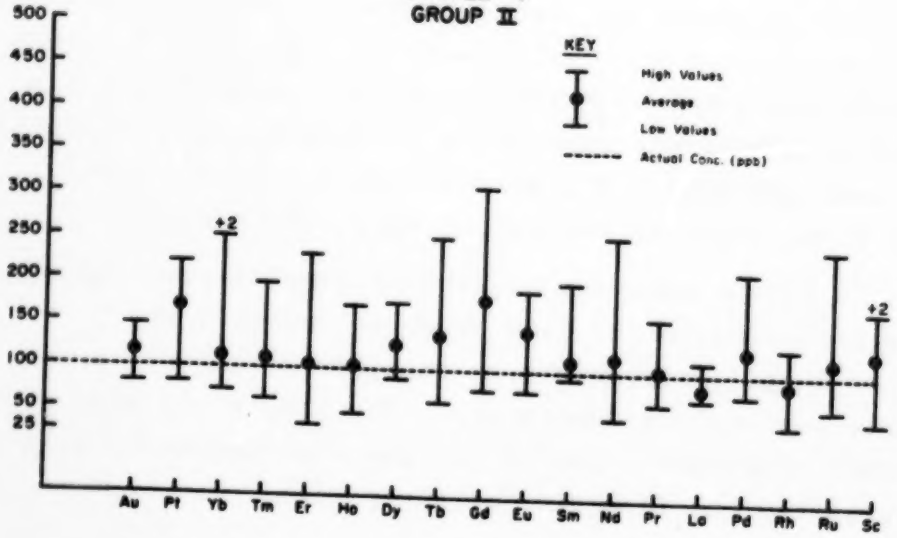
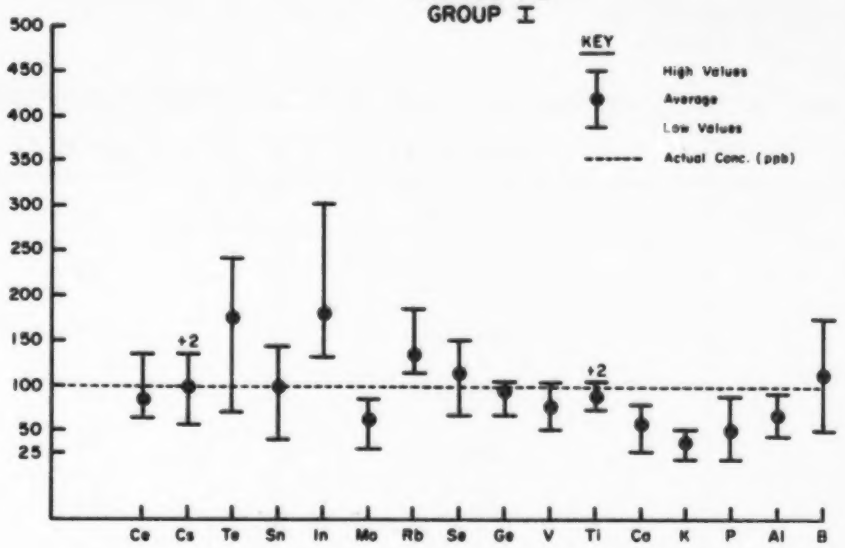


FIGURE 5
SAMPLE #2
GROUP I



SAMPLE #2
GROUP II

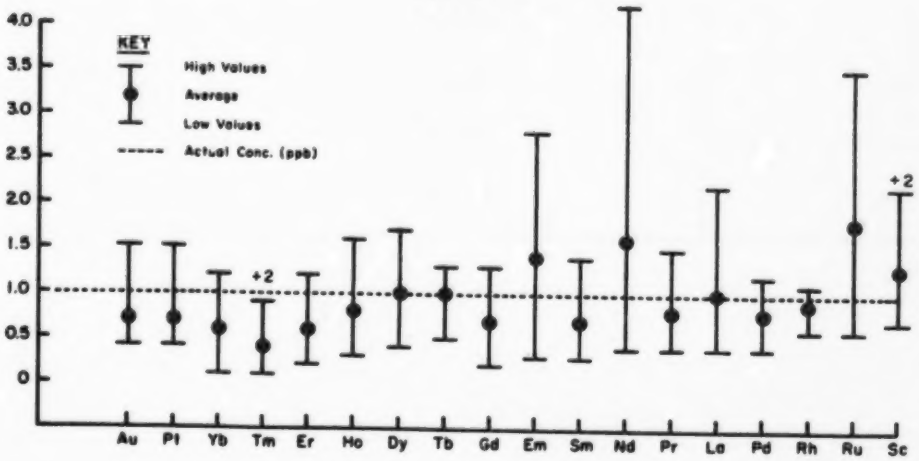


Table 1. GROUP I COEFFICIENTS OF VARIATION EXPRESSED IN PERCENT

Element	Sample #1	Sample #2
Ce	$3x10^1$	38
Cs	$2x10^1$	53
Te	$2x10^1$	73
Sn	$3x10^1$	60
In	$2x10^1$	70
Rb	$3x10^1$	38
Se	$3x10^1$	33
Ge	$2x10^1$	16
V	$3x10^1$	16
Ti	$2x10^1$	21
Ca	$1x10^1$	19
K	$5x10^1$	45
P	$6x10^1$	33
Al	$3x10^1$	31
B	$2x10^1$	33
Be	$2x10^1$	53

Table 2. GROUP II COEFFICIENTS OF VARIATION EXPRESSED IN PERCENT

Element	Sample #1	Sample #2
Au	17	$4x10^1$
Pt	27	$5x10^1$
Yb	54	$4x10^1$
Tm	38	$2x10^1$
Er	59	$4x10^1$
Ho	43	$4x10^1$
Dy	22	$4x10^1$
Tb	45	$3x10^1$
Gd	41	$3x10^1$
Eu	25	$8x10^1$
Sm	31	$4x10^1$
Nd	58	$10x10^1$
Pr	32	$3x10^1$
La	16	$6x10^1$
Pd	36	$2x10^1$
Rh	32	$4x10^1$
Ru	50	$10x10^1$
Sc	32	$4x10^1$

Table 3. ANALYSES OF EFFLUENT SAMPLE

Part I - SS Analysis of Water (Results Expressed in Parts Per Million by Weight)

Element	Avg	#1	#2	Element	Avg	#1	#2
Mg	20	27	14	Pb	0.6	0.8	0.4
P	15	15	15	Cu	0.6	0.5	0.7
Ca	10	12	8	Zn	0.5	0.6	0.4
K	9	14	6	Mn	0.3	0.4	0.2
Fe	7	7	6	Sr	0.2	0.2	0.2
Al	7	11	5	Co	0.1	0.09	0.08

Part II - SS Analysis of Major Concentration Elements in Sediment Analysis (Results in Weight Percent)

Element	Avg	#1	#2	Element	Avg	#1	#2
Fe	10	10.1	9.8	K	0.3	0.22	0.40
Mg	4	6	3	Al	0.3	0.27	0.35
Ca	2	2.9	1.8	P	0.2	0.24	0.12
Mn	0.8	1.0	0.6				

Part III - SS Analysis for the Lower Concentration Elements in Sediment (Results Expressed in Parts Per Million by Weight)

Element	Avg	#1	#2	Element	Avg	#1	#2
Sr	45	35	55	Sc	3	3.0	3.4
Ba	40	33	47	La	2	1.6	3.1
Ti	14	18	11	Sm	2	2.0	2.7
Zn	11	14	8	Cu	2	3.2	1.1
Zr	8	10	6	V	2	1.4	2.5
Ce	6	8	5	Pb	1	0.9	1.4
Y	5	6	4	Nb	1	1.4	0.4
Co	5	8	3	Rb	1	0.96	0.60
Er	3	3	3	As	1	0.5	1.5
Nd	3	3	--	Be	1	0.8	1.5
				Cs	0.5	0.5	0.47

Table 4. RELATIVE SENSITIVITY STUDY IN SEDIMENT USING INDIUM AND YTTRIUM CROSS CHECK (Established Relative Sensitivities Have Been Applied to All Results)

Part I -- Sediment Plus Standards

	Calculated Weight Percent	
Major Element	Yttrium Standard	Indium Standard
Fe	10	9
Mn	0.8	1.0
Ca	2.3	2.5
K	0.3	0.2
P	0.2	0.1
Al	0.3	0.2
Mg	4.0	4.4

Part II-- Dilution of Above Sample with More Unspiked Sample

	Calculated Concentration in ppm by Weight	
Minor Element	Yttrium Standard	Indium Standard
Ce	6	10
Ti	14	11
La	4	2
Ba	40	58
Nb	1	1
Zr	8	10
Sr	45	38

Part III--Sediment with Added Elements

Weighed amounts of these elements were added to the sediment for analysis using yttrium as the internal standard and applying relative sensitivities

	Weight Percent	
	Added	Found
Ba	6.8	7.2
Zr	4.7	4.2
Sr	3.8	3.4

milliliter water samples were spiked with yttrium as the internal standard. These were dried on graphite and compacted into electrodes for analysis. The sediment samples were dried at 110°C for two hours, weighed and spiked dry using yttrium and indium as the internal standards.

The validity of using relative sensitivity coefficients, which were obtained from very dilute solutions, in analyzing sediments was tested by two experiments. In the first of these, the sediment samples mentioned above were spiked with both yttrium and indium and analyzed using first yttrium and then indium as the internal standard. Table 4 (Parts I and II) shows a negligible difference between the values, establishing the validity of a single reference standard.

In the second experiment, relatively gross amounts of barium, strontium, and zirconium salts were added to the sediment; the sample was analyzed using the dilute-solution-derived sensitivity coefficients relative to yttrium. Results (Table 4, Part III) are in excellent agreement with the known concentrations. The relative sensitivities calculated from solutions with concentrations at the ppm levels, were therefore suitable for this analysis with concentrations in the percent range. Taken together, these two experiments indicate that, for these elements, there is no significant shift in relative sensitivity coefficients between very dilute solutions and complex sediments.

Background data from a reservoir study (Table 5) show another application of SS analysis of natural samples. The reservoir has been the site of a number of recurring fish kills. The SS data will be compared later to data

Table 5. SS ANALYSES OF RESERVOIR WATER

Element	SS	AA
Pb	2 ppb	$\leq$ 50 ppb*
Ba	160 ppb	
Ce	2 ppb	
Te	1 ppb	
Sn	10 ppb	
Cu	5 ppb	12 ppb
Ni	8 ppb	$\leq$ 50 ppb*
Co	5 ppb	
Cr	20 ppb	$\leq$ 50 ppb*
V	3 ppb	
Zn	60 ppb	40 ppb
Ti	20 ppb	
Fe	2 ppm	3.5 ppm
Mn	60 ppb	
P	30 ppb	
Sr	2 ppm	

*AA detection limit for method used

to be taken at the time of future fish kills. Comparison results with atomic absorption (AA) were available for some elements and are noted. Coefficients of variation for these SS data range from 19 to 50% and average 33% on the analysis.

SECTION VI

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